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Layer-by-layer Fabrication of Oriented Porous Thin Films Based on Porphyrin-containing Metal-organic Framework

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Given that energy migration in natural photosynthesis is generated by highlyordered porphyrin pigments (chlorophylls), equally highly ordered porphyrin-based metal–organic frameworks (MOFs) might exhibit similar behavior. Ideally a MOF-based strategy could facilitate antenna-like light-harvesting and position such materials for solar energy conversion. Previously, we reported that in a metalloporphyrin-based, pillared paddlewheel type MOF, DA-MOF, a photo-generated exciton can migrate up to 45 porphyrin struts within its lifetime and with a high anisotropy along a preferred direction. However, incorporating single crystals of DA-MOF into films, a structure relevant to solar energy conversion devices, is a significant challenge. Herein, we report the synthesis and characterization of two thin films (DA-MOF and L2-MOF) of porphyrinbased MOFs on functionalized surfaces using a layer-by-layer (LbL) approach. Profilometry measurements confirm that the film thickness increases systematically with number of growth cycles. Polarization excitation and fluorescence measurements indicate that the porphyrin units are preferentially oriented, while x-ray reflectivity scans point to periodic ordering. Ellipsometry measurements show that the films are highly porous. Since there are currently few methods capable of yielding microporous MOFs containing accessible free-base porphyrins, it is noteworthy that the LbL growth permits direct MOF incorporation of unmetalated porphyrins. Long-range energy transfer is demonstrated for both MOF films. The findings offer useful insights for subsequent fabrication of MOF-based solar-energy-conversion devices.